

VERFAHREN ZUR HERSTELLUNG VON ESTERN ORGANISCHER PHOSPHORSAEUREN

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PATENT SPECIFICATION

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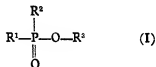
(72) Inventors PAULUS PIETER MONTIJN and HENDRIK CORNELIS KELDERMAN



(54) PREPARATION OF ORGANIC PHOSPHORUS ESTERS

(71) We, SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

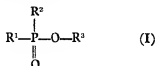
The invention relates to a process for the preparation of organic phosphorus esters of the general formula



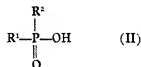
- wherein R¹ represents an organic radical, R² an organic radical or a hydrogen atom and R³ an alkyl or cycloalkyl group.

It is known from Bull.Soc.Chim.France 1966 (3), pp. 932—937, that alkyl halides react with tetramethylammonium salts of diesters of phosphoric acid and mono-esters of phosphonic acid to afford triesters of phosphonic acid and diesters of phosphonic acid, respectively. The yields in which the latter two compounds are obtained are usually moderate and occasionally very low. Applicant has now found that replacement of the alkyl halide by another alkylating agent considerably improves these yields.

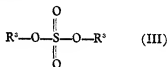
- 30 The invention may be defined as relating to a process for the preparation of organic phosphorus esters of the general formula



- wherein R¹ represents an organic radical, R² an organic radical or a hydrogen atom and R³ an alkyl or cycloalkyl group —, which process comprises the reaction of a salt of an acid of the general formula



with a dialkyl or dicycloalkyl sulphate of the general formula



in which formulas II and III R¹, R² and R³ have the above-mentioned meanings.

The yield of compounds of the general formula I are usually very high in the process according to the present invention (this process is named hereinafter the "novel process") and may even be higher than 95%.

The novel process can be performed in the absence or — which is preferred — in the presence of a solvent. Examples of suitable solvents are aliphatic hydrocarbons, such as pentanes, hexanes, heptanes, octanes, nonanes, decanes, and mixtures thereof, for example petroleum ether; cycloaliphatic hydrocarbons, such as cyclohexane, cyclooctane, decalin; aromatic hydrocarbons, such as benzene, toluene, xylenes and tetralin; ketones, such as acetone, methyl isobutyl ketone, 2-hexanone and 3-hexanone; alcohols, such as methyl alcohol, ethyl alcohol, isopropyl alcohol; chlorinated hydrocarbons, such as chloroform, methylene chloride, 1,2-dichloroethane, chlorobenzene and o-, m- and p-dichlorobenzene; nitrated hydrocarbons, such as nitromethane, nitroethane, 1-nitropropane and nitrobenzene; nitriles, such as acetonitrile; N,N-dimethylformamide, dimethyl sulphoxide and tetramethylene sulphone. Mixtures of two or more of these solvents may be applied, for example of one or more aromatic hydrocarbons and chlorinated hydrocarbons. Very good results have been obtained with aromatic hydrocarbons, N,N-dimethylformamide, chlorinated aliphatic hydrocarbons and ketones.

It is recommended that such a choice from

the salts of acids of the general formula II, the dialkyl or dicycloalkyl sulphates of the general formula III and the solvents be made that the process is performed in a homogeneous medium. This aim is generally achieved when the salts are quaternary onium salts of nitrogen, phosphorus, arsenic or antimony — in which the atoms of these four elements are bound to four substituted or unsubstituted hydrocarbyl groups —, or tertiary onium salts of sulphur, selenium or tellurium — in which the atoms of these three elements are bound to three substituted or unsubstituted hydrocarbyl groups. The hydrocarbyl groups are preferably unsubstituted. Very high yields of compounds of the general formula I have been obtained with tetrahydrocarbylammonium salts of an acid of the general formula II. The hydrocarbyl groups may, for example, be alkyl groups — whether or not substituted with cycloalkyl and/or aryl groups —, cycloalkyl groups — whether or not substituted with alkyl and/or aromatic groups — or aromatic groups — whether or not substituted with alkyl or cycloalkyl groups. Among the tetrahydrocarbylammonium salts excellent yields have been obtained with tetraalkylammonium salts, particularly when these salts have at least three alkyl groups with more than one carbon atom per group. Examples of very suitable tetraalkylammonium salts are methyltriethylammonium salts, methyl - tri - n - propylammonium salts, methyl - tri - i - butylammonium salts, methylethyl - di - n - propylammonium salts and methylethyl - n - propyl - n - butyl - ammonium salts. Excellent results have been obtained with methyltriethylammonium salts.

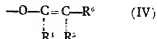
Examples of suitable tertiary onium salts are triethylsulphonium salts, di - sec - decylmethylsulphonium salts, n - hexadecyldimethylsulphonium salts, sec - dodecyl - sec - hexadecylsulphonium salts, sec - hexadecyldimethylsulphonium salts, sec - hexadecylmethylethyl sulphonium salts, trimethylsulphonium salts and di - n - butylmethylsulphonium salts.

Other examples of salts of acids of the general formula II are salts of secondary and tertiary amines, but their uses—compared with the use of quaternary onium salts—generally results in lower yields of esters of the general formula I. These yields are usually still lower when ammonium salts of acids of the general formula II are applied.

The salts of the acids of the general formula II may also be metal salts, for example salts of the alkali or alkaline earth metals, i.e. of lithium, sodium, potassium, rubidium, caesium, magnesium, calcium, strontium and barium. Among these metal salts those of potassium, rubidium and caesium are preferred.

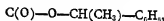
Particularly suitable as starting salts of acids of the general formula II are those in

which (a) R' represents a substituted vinyloxy group of the general formula

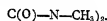


in which R' represents a hydrogen atom, a methyl group or a phenyl group optionally carrying one or more substituents, R² a hydrogen, chlorine or bromine atom and R⁶ a chlorine or bromine atom or an alkyl group with 1—5 carbon atoms, an alkoxycarbonyl group with 2 to 10 carbon atoms, an alpha-(C₁—C₆ alkyl)benzyloxycarbonyl group, a C(O)—O—CH(C₁—C₆ alkyl)phenyl, or a substituted carbamoyl group C(O)—NR'R³ in which R' represents a hydrogen atom or an alkyl group with 1—5 carbon atoms, and R³ an alkyl group with 1—5 carbon atoms, and (b) R² represents an alkyl group with 1—5 carbon atoms or an alkoxy group with 1—10 carbon atoms.

Examples of substituents when R' represents a phenyl group are fluorine, chlorine and bromine atoms—for example as present in 2,4- or 2,5-dichlorophenyl or 2,4,5-trichlorophenyl groups —, cyano groups and alkoxy groups, such as methoxy and ethoxy groups. R³ may, for example, represent an alpha-methylbenzyloxycarbonyl, i.e.

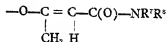


or a substituted carbamoyl group such as N-methylcarbamoyl i.e. C(O)—NH(CH₃), or N,N-dimethylcarbamoyl, i.e.



In a very suitable class of starting salts R' represents a hydrogen atom and R² a chlorine or bromine atom, especially chlorine, where R' may also be hydrogen. Very good results have been obtained where R¹ and R⁶ each separately represent a chlorine atom.

In another very suitable class of starting salts of acids of the general formula II R' represents a substituted vinyloxy group of the general formula



in which R⁷ and R⁸ have the above-mentioned meanings.

Examples of such starting salts that have proved particularly suitable are those in which R⁷ represents a hydrogen atom or a methyl group and R⁸ a methyl group.

A particularly suitable class of starting salts of acids of the general formula II comprises those wherein R¹ in formula IV represents a phenyl or substituted phenyl group and R²

a chlorine or bromine atom or a C₁—C₂ alkyl group. Excellent results are achieved, for example, when R¹ represents a halogenated—preferably chlorinated—phenyl group, particularly 2,4-dichlorophenyl, 2,5-dichlorophenyl, or 2,4,5-trichlorophenyl. Either or both of the substituents R² and R³ preferably represent a chlorine atom. If only one of these is chlorine, R² is preferably a hydrogen atom.

- 10 Another very suitable class of starting salts of acids of the general formula II comprises those in which R¹ (see formula IV) represents a methyl group, R² a hydrogen atom and R³ a methoxy-carbonyl group.

- 15 R² in the salts of the acids of the general formula II, may, for example, represent a methyl, ethyl, ethoxy or—which is preferred—a methoxy group.

- 20 Examples of suitable dialkyl sulphates of the general formula III are dimethyl sulphate, diethyl sulphate, dipropyl sulphate, dibutyl sulphate, dipentyl sulphate, dihexyl sulphate, diheptyl sulphate, dioctyl sulphate, dinonyl sulphate, didecyl sulphate, didodecyl sulphate, 25 ditetradecyl sulphate and dioctadecyl sulphate. Very good results have been obtained with diethyl sulphate.

- The process of the invention has proved to be very useful for the preparation of various substituted vinyl esters of acids of phosphorus having improved biocidal, especially insecticidal, acaricidal and/or anthelmintic, for example nematocidal, properties. Examples of very useful organic phosphorus esters of the general formula I obtained according to the novel process using an appropriate dialkyl sulphate as compound of the general formula III are: methyl ethyl [2-chloro - 1 - (2,4,5 - trichlorophenyl)]vinyl-phosphate; methyl ethyl [2 - chloro - 1 - (2,4-dichlorophenyl)]vinyl phosphate; methyl ethyl 2,2-dichlorovinyl phosphate; methyl ethyl (1-methyl - 2 - N - methylcarbamoyl)]vinyl phosphate, methyl ethyl(1 - methyl - 2 - metha- 45 carbonyl)]vinyl phosphate, methyl n-butyl 2,2-dichlorovinyl phosphate and methyl n-butyl [2 - chloro - 1 - (2,4 - dichlorophenyl)]-vinyl phosphate.

- Generally, reaction temperatures of from 25 to 100° C. have been found to be very suitable, temperatures of from 40 to 75° C. being preferred as a rule, because the selectivity to the compound of the general formula I is usually highest in the latter range, and, the conversion of the salts of the acids of the general formula II being very high, also the yield of the compound of the general formula I. The selectivity in %mol to a particular compound is defined herein as the number of moles of the salt of the acid of the general formula II that have been converted into this particular compound multiplied by 100 and divided by the total number of converted moles of this salt. Consequently, the yield of a particular compound is the

selectivity to this compound multiplied by the conversion (in %) of the salt of the acid of the general formula II and divided by 100.

The salt of the acid of the general formula II and the compound of the general formula III can be caused to react in a molar ratio II:III which is not critical and may vary within wide limits. It is recommended that this molar ratio be maintained at a value lower than 1 because at values higher than 1 the conversion of the salt will be correspondingly low. Generally, molar ratios between 1:1 and 1:1.5 are very suitable and in many cases very high yields of compounds of the general formula I are obtained at molar ratios between 1:1 and 1:1.2.

The compound of the general formula I may be isolated from the reaction mixture in any desired manner. A very suitable manner is extracting unreacted salt of the acid of drying the raffinate phase obtained and distilling off the solvent and unreacted compound of the general formula III. The distillation residue obtained usually has a content of the compound of the general formula I of between 90 and 95%. Preferably the novel process is performed in the presence of a water-immiscible solvent, because these solvents make the said extraction of the reaction mixture with water possible. It has been found that toluene is a very suitable solvent.

The novel process can be performed by stirring a heated solution containing the salt of the acid of the general formula II and the compound of the general formula III for, say, 1.5–5 hours. Quaternary ammonium salts of phosphoric acids of the general formula II, in their turn are also easily formed, viz. by causing a triester of phosphoric acid to react with a tertiary amine, preferably in the presence of a solvent. A preferred embodiment of the present invention, therefore, comprises the reaction of a compound of the general formula



(V)

—wherein R¹ and R² are ester-forming radicals having above-mentioned meanings—with a tertiary amine, keeping the quaternary salt of the acid of the general formula II thus formed in the reaction mixture and the reaction of this salt with a compound of the general formula III according to the novel process, in which formula III R³ does not represent a methyl group.

Alkali metal or alkaline earth metal salts of phosphoric acids of the general formula II are also easily formed, viz. by causing a triester of phosphoric acid to react with an

alkali metal or alkaline earth metal cyanide, acetate, halide or—which is preferred—thiocyanate, preferably in the presence of a solvent. Another preferred embodiment of the present invention, therefore, comprises the reaction of a compound of the general formula V with a thiocyanate of an alkali metal or of an alkaline earth metal, keeping the alkali metal or alkaline earth metal salt of the acid of the general formula II thus formed in the reaction mixture and the reaction of this salt with a compound of the general formula III in which R³ is not methyl according to the novel process. An advantage of the latter embodiment is the very high purity, for example 98—99%, in which the compounds of the general formula I are usually obtained.

The invention is further illustrated by means of the following Examples. Each example presents data on the conversion of a trihydrocarbyl phosphate with an amine or a salt into a salt of a dihydrocarbyl phosphate and of the conversion of this dihydrocarbyl phosphate salt with an alkylating agent into a trihydrocarbyl phosphate different from the starting trihydrocarbyl phosphate. Both conversions were performed in a stirred reaction mixture. These data include the reactants, the amounts of the reactants, the solvent, the amount of the solvent, the reaction temperatures and the reaction times applied. The parts of the Tables I—V left and right from the dotted vertical line relates to the reaction of the starting trihydrocarbyl phosphate and of the resulting dihydrocarbyl phosphate salt, respectively. Dimethyl 2 - chloro - 1 - (2,4-dichlorophenyl)vinyl phosphate, where used as the starting trihydrocarbyl phosphate, is denoted below with "compound I" and has a purity of 99%. After the reaction of the salt with the alkylating agent the solvent was flashed off—except where toluene was used as the solvent—and 70 ml toluene was added to the distillation residue obtained. Un-

reacted dihydrocarbyl phosphate salt was removed from the toluene-containing liquid thus obtained by extracting three times with 50 ml water. The raffinate phase thus formed was separated from the extract phase, dried over sodium sulphate and subjected to distillation at a pressure of 0.0013 bar to remove the toluene. Subsequently, the content of the product trihydrocarbyl phosphate in the distillation residue formed was determined; this content is indicated by "purity" in the tables I—V.

EXAMPLE I.

In experiments 1—7 0.100 mol of compound I was reacted with 0.105 mol triethylamine using various solvents at a temperature of 60° C. to afford methyltriethylammonium methyl - 2 - chloro - 1 - (2,4 - dichlorophenyl)vinyl phosphate (below denoted by "compound II"). When the reaction of the experiments 1, 2, 3, 5 and 7 was terminated the solvent was flashed off at a pressure of 0.02 bar abs. In experiment 4 the solvent was kept in the solution. Then, the experiments 8—14 were performed in which the distillation residues formed in the experiments 1—3 and 5—7 and the solution of experiment 4 were reacted with 0.110 mol diethyl sulphate. To the distillation residue of experiment 1 40 ml N,N-dimethylformamide was added. The acetone present at the start of experiment 11 was distilled off when adding diethyl sulphate. The reaction mixture underwent a considerable viscosity decrease during the reaction with diethyl sulphate. Table I states the other relevant data, the conversion of compound I, the selectivities to methyl ethyl 2 - chloro - 1 - (2,4 - dichlorophenyl)vinyl phosphate (below denoted by "compound III") and to diethyl 2 - chloro - 1 - (2,4-dichlorophenyl)vinyl phosphate (below denoted by "compound IV"). The time started for reaction with diethyl sulphate includes 0.5 hour for addition of diethyl sulphate.

Table I.

Exp. No.	solvent	amount of solvent, ml	stirring time, h	Exp. No.	temp., °C	reaction time, h	conversion, %	selectivity (%) to compound		purity of compound III, %
								III	IV	
1	toluene	40	3	8	65	19	93.8	94.1	less than 1.1	92.1
2	N,N-dimethyl-formamide	40	3	9	80	2	94.7	91.3	6.4	87.9
3	1,2-dichloro-ethane	40	3	10	80	2	96.9	94.8	2.1	90.6
4	acetone	40	3	11	80	2.5	83.7	95.7	0.8	80
5	toluene	40	5	12	80	2.5	87.5	94.1	4.9	81.5
6	none	0	2.5	13	80	1.75	96.5	90.0	7.8	84.7
7	toluene	5	3	14	60	2	97.0	97.3	2.7	92.4

EXAMPLE II.

In experiments 1-7 (see Table II) compound I was reacted with triethylamine in the presence of 15 %w of toluene, calculated on compound I. The reaction mixtures formed in experiments 1-4 were reacted with diethyl sulphate, that formed in experiment 5 with di-n-butylsulphate and those formed in the comparative experiments 6 and 7 with ethyl iodide. Table II states the other relevant data; the reaction times stated include one hour for the addition of triethylamine and diethyl sulphate. Table II also presents the conversion of compound I, the selectivities to compounds III and IV and the purity of compound III.

Table II.

Exp. No.	amount, mol		temp., °C	reaction time, h	Exp. No.	amount of diethyl sulphate	temp., °C	reaction time, h	conversion, %	selectivity (%) to compound		purity of compound III, %w
	compound I	triethyl amine								III	IV	
1	0.667	0.700	70	2	8	0.733	50	4	98.4	95.3	2.0	92.8
2	0.0905	0.095	70	2	9	0.095	50	4.5	97.1	96.3	3.7	93.9
3	0.100	0.105	60	2	10	0.110	90	1.75	92.4	85.7	10.3	80.0
4	0.100	0.105	90	1	11	0.110 di-n-butyl sulphate	60	2	99.3	95.3	1.5	94.5
5	0.0700	0.0735	50	5.5	12	0.0735 ethyl iodide, mol	50	5	94	95*	3**	79.5
6	0.100	0.105	70	2	13')	0.110	90	2	88.9	48.2	32.3	49.4
7	0.100	0.105	70	2	14'	0.110	50	3.5	91.6	72.3	15.4	74.4

'), not according to the invention.

* Yield of n-butyl methyl 2-chloro-1-(2,4-dichlorophenyl)vinyl phosphate.

** Yield of di-n-butyl 2-chloro-1-(2,4-dichlorophenyl)vinyl phosphate.

EXAMPLE IV.

In experiments 1-8 (see Table IV) 0.1 mol of compound 1 was reacted with various salts in the presence of 20 ml N,N-dimethyl-5 formamide. The reaction mixtures formed in experiments 1 and 3-8 were reacted with diethyl sulphate and that formed in comparative experiment 2 with ethyl chloride.

Table IV states the other relevant data and reaction conditions. The time for reaction with diethyl sulphate includes 0.35 hour for the addition of this sulphate. Table IV also presents the conversion of compound I; the selectivities to compounds III and IV and the purity of compound III.

Table IV.

Exp. No.	salt	amount of salt, mol	temp., °C	reaction time, h	Exp. No.	alkylating agent	amount of alkylating agent, mol	temp., °C	reaction time, h	conversion, %	selectivity, % to III	selectivity, % to IV	purity of III, %
1	NaCN	0.105	90	3	9	diethyl sulphate	0.105	60	4½	97.7	75.3	0.6	90.3
2	NaCN	0.105	70	4	10	ethyl chloride ¹⁾	0.195	90	5½	98.5	5.5	0.2	—
3	KSCN	0.105	90	4	11	diethyl sulphate	0.105	60	5½	99.8	83.5	1	94.9
4	KSCN	0.105	60	5	12	ditto	0.105	60	5½	99.3	89.7	0.7	98.5
5	NaCl	0.105	120	4	13	ditto	0.105	60	4½	59.7	38.5	22.6	27.3
6	NaCl	0.105	70	4	14	ditto	0.105	60	4½	4.3	55.8	0	—
7	CH ₃ COOK	0.105	70	6	15	ditto	0.105	70	6	88.1	73.4	0	81.0
8	triethylamine hydrochloride	0.105	70	5	16	ditto	0.105	70	5½	99	76	0.8	97.4

¹⁾ not according to the invention.

EXAMPLE V.

In experiments 1-5 (see Table V), various dimethyl phosphates were reacted with 0.105 mol triethylamine, in the experiments 1-3 in the presence of 15 ml of toluene and in experiment 5 of 5 ml of toluene and in experiment 4 of 20 ml of N,N-dimethylformamide. In experiment 6 0.0735 mol triethylamine and 5 ml toluene were used. The reaction mixtures formed in experiments 1, 2, 4 and 5 were reacted with 0.105 mol di-

ethyl sulphate, that formed in experiment 6 with 0.073 mol diethyl sulphate and that formed in comparative experiment 3 with 0.105 mol hexyl bromide. Table V states the other relevant data and reaction conditions; the reaction times include 0.5 hour for the addition of triethylamine and diethyl sulphate. Table V also presents the conversions of the starting dimethyl phosphate and the yield and purity of the corresponding methyl ethyl phosphate.

Table V.

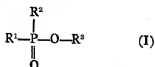
Exp. No.	starting dimethyl phosphate	amount of starting phosphate, mol	temp., °C	reaction time, h	Exp. No.	temp., °C	reaction time, h	methyl ethyl phosphate obtained:	
								yield, %	purity, %
1	dimethyl 1-(2,4,5-trichlorophenyl)-2-chlorovinyl phosphate	0.100	70	4½	7	50	4½	more than 90	more than 90
2	dimethyl 2,2-dichlorovinyl phosphate	0.100	50	4	8	50	4½	90	90
3	ditto	0.100	50	5	9 ¹⁾	50 and then 80	5 and then 3/4	5	35
4	dimethyl 1-(1-methyl-2-(N-methyl-carbamoyl)vinyl) phosphate	0.110	50	4½	10	50	6	more than 85	more than 40
5	dimethyl 1-methyl-2-methoxy-carbonylvinyl phosphate	0.100	50	5½	11	50	5½	more than 85	90
6	dimethyl 2,2-dichlorovinyl phosphate	0.070	50	5½	12	50	5½	86	74.6

¹⁾ not according to the invention.

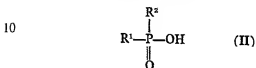
The unreacted dihydrocarbyl phosphate was not removed from the reaction mixture, obtained in experiment 10, resulting in the low purity of more than 40% of the product methyl ethyl phosphate.

WHAT WE CLAIM IS:—

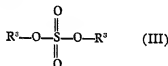
1. A process for the preparation of organic phosphorus esters of the general formula



5 —wherein R¹ represents an organic radical, R² an organic radical or a hydrogen atom and R³ an alkyl or cycloalkyl group, which process comprises the reaction of a salt of an acid of the general formula



10 with a dialkyl or dicycloalkyl sulphate of the general formula



15 in which formulas II and III R¹, R² and R³ have the above-mentioned meanings.

2. A process as claimed in claim 1, in which as salt of the acid of the general formula II a tetrahydrocarbylammonium salt is used.

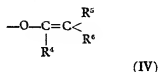
20 3. A process as claimed in claim 2, in which as tetrahydrocarbylammonium salt a tetraalkylammonium salt is used.

4. A process as claimed in claim 3, in which a tetraalkylammonium salt is used having at least three alkyl groups with more than one carbon atom per group.

25 5. A process as claimed in claim 4, in which as tetraalkylammonium salt a methyl-triethylammonium salt is used.

30 6. A process as claimed in claim 1, in which as salt of the acid of the general formula II a potassium, rubidium or caesium salt is used.

35 7. A process as claimed in any one of the preceding claims, in which in the salt of the acid of the general formula II (a) R¹ represents a substituted vinyloxy group of the general formula



40 in which R⁴ represents a hydrogen atom, a methyl group or a phenyl group optionally

carrying one or more substituents, R⁶ a hydrogen, chlorine or bromine atom and R⁵ a chlorine or bromine atom or an alkyl group with 1—5 carbon atoms, an alkoxy-carbonyl group with 2 to 10 carbon atoms, and alpha-(C₁—C₂ alkyl)benzyloxycarbonyl group C(O)—O—CH (C₁—C₂ alkyl)-phenyl, or a substituted carbamoyl group

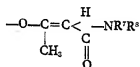


in which R⁷ represents a hydrogen atom or an alkyl group with 1—5 carbon atoms, and R⁸ is an alkyl group with 1—5 carbon atoms, and (b) R² represents an alkyl group with 1—5 carbon atoms or an alkoxy group with 1—10 carbon atoms.

8. A process as claimed in claim 7, in which in the substituted vinyl group of the general formula (IV) R⁴ represents a hydrogen atom and R⁵ a chlorine or bromine atom.

9. A process as claimed in claim 8, in which R⁶ and R⁵ each separately represent a chlorine atom.

10. A process as claimed in claim 7, in which R¹ represents a substituted vinyloxy group of the general formula



in which R⁷ and R⁸ have the above-mentioned meanings.

11. A process as claimed in claim 10, in which R⁷ represents a hydrogen atom or a methyl group and R⁸ a methyl group.

12. A process as claimed in claim 7, in which R¹ represents a phenyl or substituted phenyl group and R⁵ a chlorine or bromine atom or a C₁—C₂ alkyl group.

13. A process as claimed in claim 12, in which R⁴ represents a halogenated phenyl group.

14. A process as claimed in claim 13, in which the halogenated phenyl group is a 2,4- or 2,5-dichlorophenyl or 2,4,5-trichlorophenyl group.

15. A process as claimed in any one of claims 12—14, in which R⁷ represents a hydrogen or a chlorine atom and R⁸ a chlorine atom.

16. A process as claimed in claim 7, in which R⁴ represents a methyl group, R⁵ a hydrogen atom and R⁶ a methoxycarbonyl group.

17. A process as claimed in any one of claims 7—16, in which R² represents a methoxy group.

18. A process as claimed in any one of the preceding claims, in which as dialkyl sul-

phate of the general formula III diethyl sulphate is used.

19. A process as claimed in any one of the preceding claims, which is performed at a temperature in the range of from 25 to 100° C.

20. A process as claimed in claim 19, which is performed at a temperature in the range of from 40 to 75° C.

21. A process as claimed in any one of the preceding claims, in which the salt of the acid of the general formula II and the compound of the general formula III are applied in a starting molar ratio II:III between 1:1 and 1:1.5.

22. A process as claimed in any one of the preceding claims, which is performed in the presence of a water-immiscible solvent.

23. A process as claimed in claim 22, in which as solvent toluene is used.

24. An integrated process for the preparation of organic phosphorus esters of the general formula I, which process comprises the reaction of a compound of the general formula



(V)

- wherein R¹ and R² are ester forming radicals having the above-mentioned meanings—with a tertiary amine, keeping the quaternary ammonium salt of the acid of the general formula II thus formed in the reaction mixture and causing this salt to react with a compound of the general formula III according to any one of the preceding claims, in which formula III R³ does not represent a methyl group.

25. An integrated process for the preparation of organic phosphorus esters of the general formula I, which process comprises the

reaction of a compound of the general formula



(V)

—wherein R¹ and R² are ester forming radicals having the above mentioned meanings—with a thiocyanate of an alkali metal or of an alkaline earth metal, keeping the alkali metal or alkaline earth metal salt of the acid of the general formula II thus formed in the reaction mixture and causing this salt to react with a compound of the general formula III wherein R³ does not represent a methyl group according to any one of claims 1, and 6 to 23.

26. A process for the preparation of organic phosphorus esters substantially as hereinbefore described, with special reference to Example I, Example II experiments 8—12 separately and the five combinations 1 and 8, 2 and 9, 3 and 10, 4 and 11 and 5 and 12, Example III, Example IV, experiments 9 and 11—16 separately and the seven combinations 1 and 9, 3 and 11, 4 and 12, 5 and 13, 6 and 14, 7 and 15, and 8 and 16, and Example V experiments 7, 8, 10, 11 and 12 separately and the five combinations 1 and 7, 2 and 8, 4 and 10, 5 and 11 and 6 and 12.

27. Organic phosphorus esters of the general formula I whenever prepared by a process as claimed in any one of the preceding claims.

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